Supercapacitor charge and self-discharge analysis

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INTRODUCTION

Supercapacitor is the electronic device, which can store a huge amount of energy. The capacity up to the order of thousand Farads and relatively short charging time gives the possibility to use supercapacitors as an extra power source. The detail study of the supercapacitor charge and self-discharge processes were performed. Similar research was provided in [1 to 4].

The charge on the supercapacitors with carbon electrodes is stored not only in Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte. After the quick charging of the Helmholtz capacitance, the charge in the supercapacitor is redistributed by diffusion process which leads to the increase of total capacitance of the sample. On the base of study of the time dependence of voltage on the supercapacitor terminals we have observed, that the diffuse capacitance in the supercapacitor is charged within the time interval of the order of hundreds seconds. The increase of capacitance due to the charging of the diffuse capacitance leads to the decrease of voltage on the supercapacitor terminals.

Supercapacitor self-discharge analyzes is based on the physical reasoning of Helmholtz and diffuse layer capacitances. Voltage on the terminals decreases at first exponentially with time for time interval up to 10^4 s. In this case the Helmholtz layer is the main source of electric charges for the self-discharging process. Then potential gradient between the Helmholtz and the diffuse layers appears and electric charge is supplied from the diffuse layer too. Discharge time characteristic is described by the exponential stretched law with the exponent n in the range 1 to 0.5, while for the time interval longer than 10^6 s is changed into the pure diffusion law with the exponent $n = 0.5$. The equivalent circuit model consists of two *RC* branches, one of them representing the Helmholtz layer and the second one representing the diffuse layer with a time dependent resistance is proposed. A method to identify the equivalent circuit parameters will be presented.

SAMPLES AND EXPERIMENT

Two sets of commercially produced supercapacitors were evaluated. The first ones, denoted as M, were supercapacitors Maxwell 10 F/2.5 V – the set of 10 pcs; the second ones, denoted as N, were supercapacitors NessCap 10 F/2.7 V – the set of 10 pcs.

In the first experiment the samples were charged into the nominal voltage 2.5 V, and 2,7 V, respectively, for the time interval 3 days (about 2.6 x 10^5 s) in order to charge both the Helmholtz and Diffuse capacitances. Then they were kept on the open circuit and the voltage on the capacitor terminals was monitored within the time interval up to 3 x 10^6 s (about 35 days) for N samples, and time interval up to 6 x 10^6 s (about 70 days) for M samples, respectively (see Figs. 1 and 2). About 10 measurements were provided during this period so the discharge via the measuring voltmeter is negligible.

Further we have performed the second experiment in which the value of Helmholtz and Diffuse capacitance can be determined. In this experiment capacitor is charged by current $I = 2$ A for the time interval 10 s (see Fig. 3) and then the voltage on capacitor is measured for time interval 2000 s (see Fig. 4). We suppose that total electric charge $Q_T = 20$ C is stored in Helmholtz capacitance only during the charging process. Voltage on the capacitor decreases during the monitored time interval from the value $U_0 = 2.3$ V due to that the diffuse layer capacitance is charged. We consider the total electric charge Q_T as constant during the whole experiment. Electric charge loss due to the current leakage can be neglected. The leakage current is less than 10 μA for our samples and during the time interval 2000 s the charge loss Q_L is less than 20 mC.

All experiments were performed at the temperature 25°C.

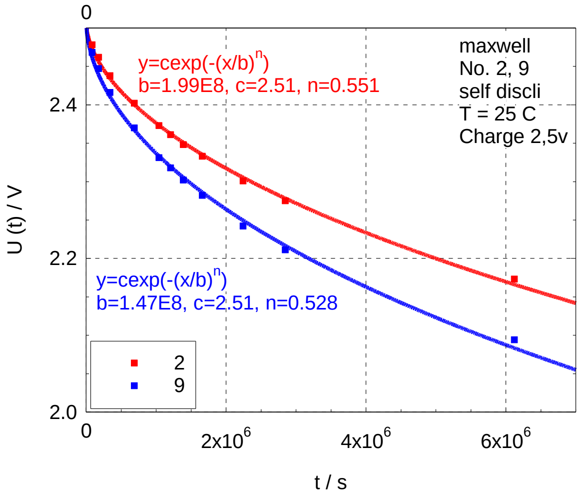

Fig. 1. Self-discharge current time dependence for two samples (M-2 – upper line, M-9 – lower line) of supercapacitors

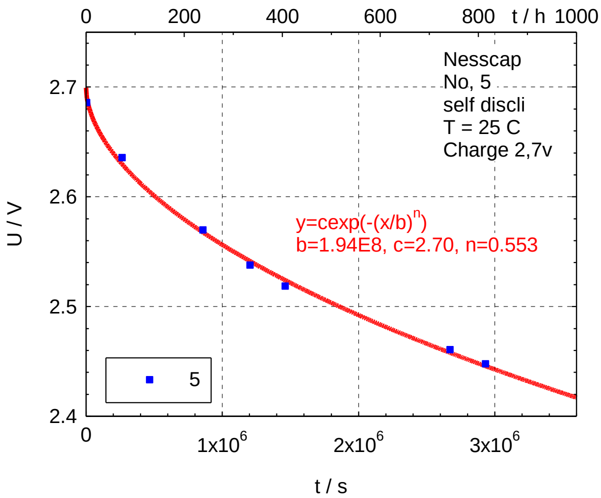

Fig. 2. Self-discharge current time dependence for supercapacitor sample N-5

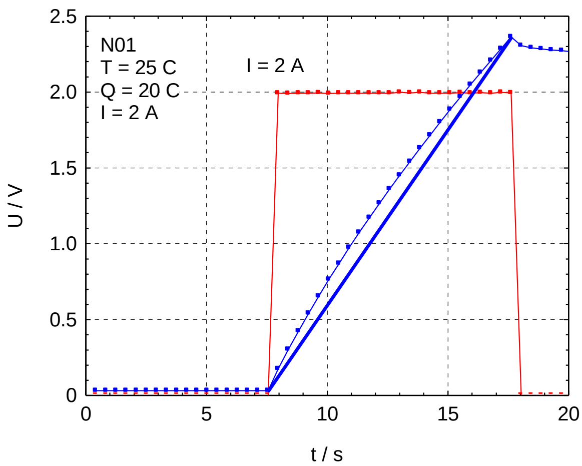

Fig. 3. Time dependence of voltage on terminals of supercapacitor sample N-1 (blue line). Further is shown the time dependence of charging current pulse - upper value is 2 A (red line)

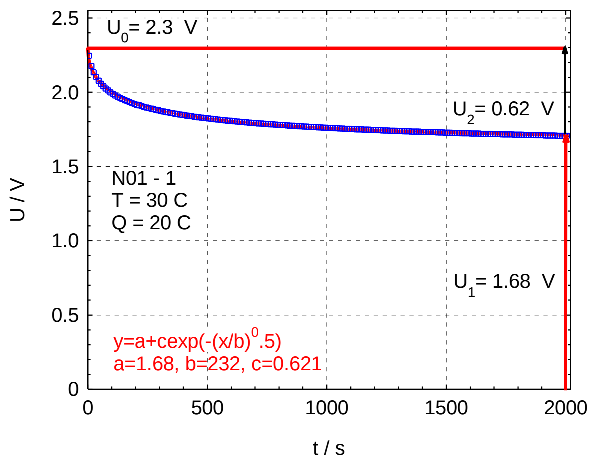

Fig. 4. Time dependence of voltage on terminals of supercapacitor sample N-1

HELMHOLZ AND DIFFUSE CAPACITANCE VALUES ESTIMATION

Electric charge stored in Helmholtz capacitance reacts immediately on the voltage change on electrodes and electric charge change dQ_H is proportional to the charge on this capacitance and the time change dt:

$$dQ_H = Q_H \frac{dt}{\tau_1} \quad (1)$$

Where Q_H is the charge on Helmholtz capacitance C_1 and τ_1 is the time constant which is given by the value of Helmholtz capacitance C_1 and capacitor series resistance.
Electric charge stored in Diffuse capacitance reacts on the voltage change on electrodes with some time delay due to the motion of electric charges by diffusion. The time dependence of the electric charge change dQ_D is proportional to the charge Q_D and time change dt divided by the root from time multiplied by the time constant τ_2 :

$$dQ_D = Q_D \frac{dt}{2\sqrt{t \cdot \tau_2}} \quad (2)$$

Where Q_D is charge on Diffuse capacitance and τ_2 is the time constant for electric charge diffusion.
Time dependence of voltage on capacitor terminals (see Fig. 4) could be fitted by:

$$U(t) = U_1 + U_2 \exp(-(t/\tau_2)^{0.5} \quad (3)$$

Where the voltage $U_0 = U_1 + U_2 = 2.3$ V is the voltage measured immediately after the capacitor charging for $t = 0$ s, voltage $U_1 = 1.68$ V is the value on the voltage terminals after the charging of Diffuse capacitance, the voltage $U_2 = 0.62$ V represents the voltage drop on the capacitor terminals within the time interval 2000 s, and the time constant $\tau_2 = 232$ s.
From the evaluated values of voltage on the supercapacitor terminals the values of Helmholtz and diffuse capacitance, respectively, can be calculated.
Helmholtz capacitance C_H is charged immediately and depends on the total charge $Q_T = 20$ C and on the voltage U_0. It is given as $C_H = Q_T/U_0$, for sample N-1we have $C_H = 8.7$ F.
Total capacitance at the end of studied time interval depends on the total charge $Q_T = 20$ C and on the voltage U_1. It is given as $C_T = Q_T/U_1$, for sample N-1we have $C_T = 11{,}9$ F. Total capacitance is a sum of the Helmholtz and Diffuse capacitances $C_T = C_D + C_H$.
Then the Diffuse capacitance can be calculated as $C_D = C_T - C_H$; for sample N-1we have $C_D = 3.2$ F.

Table 1. Helmholtz, Diffuse and total capacitances calculated for sample of set N

Sample No.	C_H / F	C_D / F	C_T / F
N-1	8.7	3.2	11.9
N-2	8.8	3.45	12.27
N-3	8.8	3.32	12.12
Average value	8.77	3.33	12.097

The values of Helmholtz, Diffuse and total capacitance measured for three samples of set N are shown in Table 1. We can see, that the technology is well reproducible and the Diffuse capacitance is about one half of the Helmholtz one. These results are important from the point of view of supercapacitor equivalent circuit modeling for the estimation of the equivalent circuit parameters values.

SUPERCAPACITOR SELF-DISCHARGING ANALYSIS

Self-discharge current time dependence can be fitted by the equation

$$U(t) = U_0 \exp(-(t/\tau)^n \tag{4}$$

Where an exponent value n = 1 for the time interval up to 1000 s (see Fig. 5), n = 0.73 for time interval up to 5 x 10^4 s (see Fig. 6), while $n \approx 0.5$ in the long time period up to 6 x 10^6 s (see Figs. 1 and 2). Exponent value 1 corresponds to the discharge of ideal capacitor through the resistor R_p, which in our case is represented by the equivalent parallel resistance of the capacitor leakage. Then the time constant $\tau = R_p C_H$. From the fit in Fig. 5 it follows, that the value of R_p is about 113 kohm, and then the initial leakage current value is 22 μA.

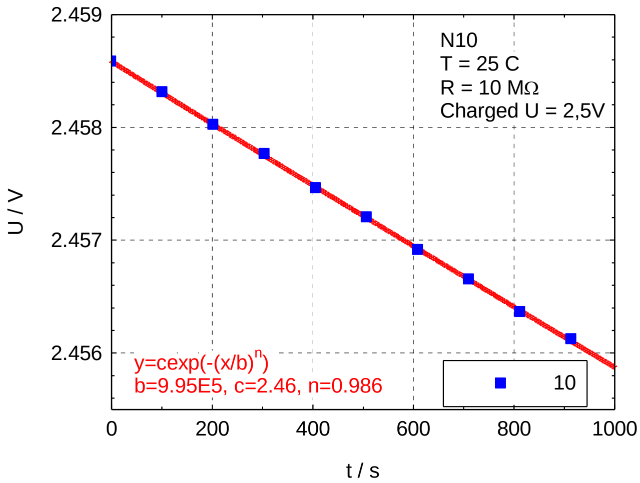

Fig. 5. Time dependence of voltage on terminals of supercapacitor sample N-10, measured values (blue squares) and mathematical model (red line)

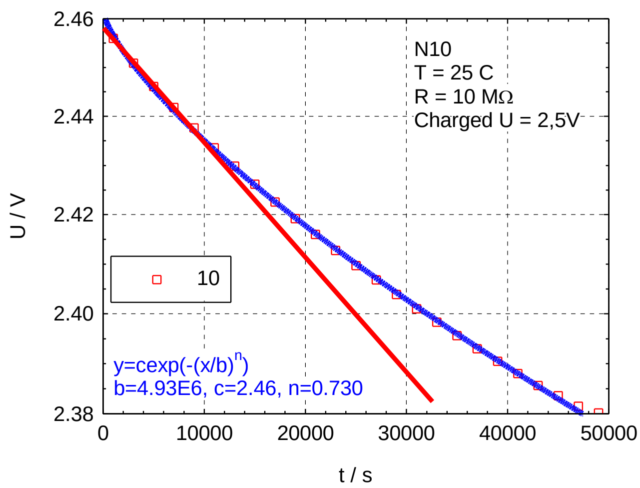

Fig. 6. Time dependence of voltage on terminals of supercapacitor sample N-10, measured values (red squares) and mathematical model (blue line)

With wider time interval the value of exponent n decreases, due to that the diffusion process is involved in the capacitor self-discharge, up to reaching the value n = 0.5 which corresponds to the pure diffusion process. The time constant value increases with time, because the time dependent value of resistance R_2, responsible for the self-discharge of diffuse capacitance increases with time as well.

The time dependence of the time constant is shown in Fig. 7 for the time interval up to 5 x 10^4 s. Time constant value increases with the time interval of the measurements linearly first and then the sub-linearly, when the diffusion process become dominant.

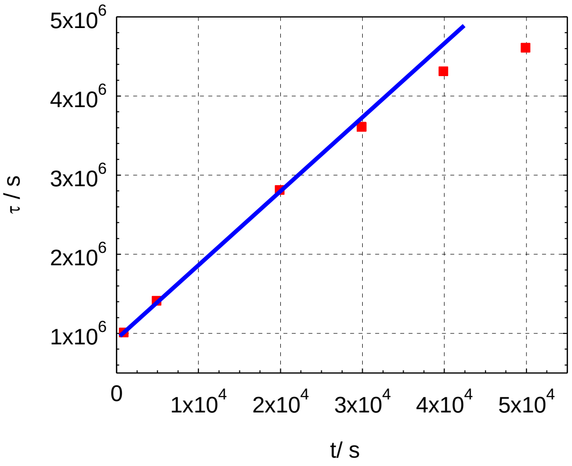

Fig. 7. Time dependence of time constant value of supercapacitor sample N-10

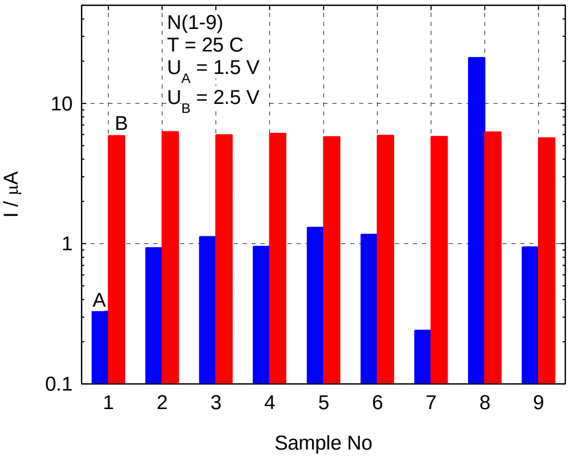

Fig. 8. Leakage current value for voltages 1.5 V and 2.5 V measured after 100 hours of self-discharge - ensemble N

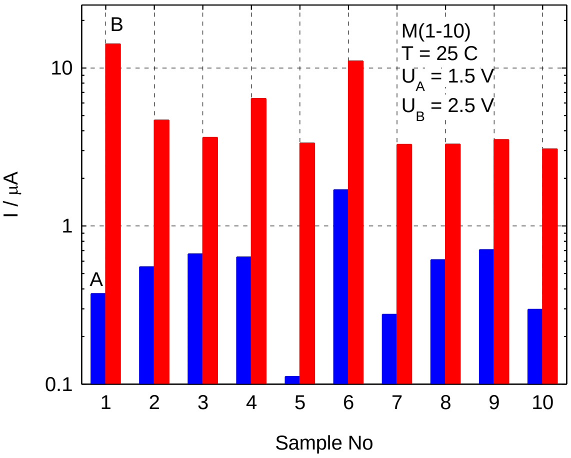

Fig. 9. Leakage current value for voltages 1.5 V and 2.5 V measured after 100 hours of self-discharge - ensemble M

The leakage current value is influenced by the potential barriers formed on the carbon-electrolyte interface and by the resistance of the supercapacitor structure [1]. In the case that the supercapacitor structure resistance is dominant, linear dependence between the leakage current and voltage on the supercapacitor terminals can be expected. In Figs. 8 and 9 the leakage current values for voltages 1.5 V and 2.5 V measured after 100 hours of self-discharge for all the samples of ensembles N and M are shown. The leakage current mean values and standard deviations calculated for the voltage 1.5 V is 0.876 μA for ensemble N, and 0.593 μA for ensemble M, and for the voltage 2.5 V is 5.965 μA for ensemble N, and 5.648 μA for ensemble M (see Tab. 2). For the voltage increase for 67 % we observed, that the current increased about 7 times for ensemble N and about 10 times for ensemble M. This nonlinear dependence of leakage current cannot be driven by the resistance. We suppose that dominant parameter influencing the leakage current value is the barrier on the interface between the carbon electrode and electrolyte. On the basis of Schottky electron transport we estimate this barrier value for about 1.5 eV.

Table 2. The leakage current mean values and standard deviation calculated for samples of sets M and N, respectively

	Maxwell		NessCap	
	U = 1.5 V	U = 2.5 V	U = 1.5 V	U = 2.5 V
Mean value / μA	0.59	5.64	0.87	5.96
Standard dev. / μA	0.43	3.88	0.38	0.21

CONCLUSIONS

The time dependences of voltage on the supercapacitor terminals after the charging for 3 days due to the self-discharge were studied. Self-discharge process can be divided into two regions; (i) for time interval less than 10^4 s voltage decreases exponentially with time as for ideal capacitor. Time constant of this process is of the order of 1 x 10^6 s. From the time constant value the equivalent parallel resistance of the capacitor leakage was calculates, and it is of the order of 100 kohm. The initial leakage current value is about 20 μA and decreases down to about 5 μA for the bias voltage 2.5 V. The leakage current dependence on the bias voltage is non-linear and then we suppose that the current is driven by the potential barrier formed on the carbon electrode – electrolyte interface. (ii) For the long time interval up to 1000 hours self-discharge process is controlled by the electric charge diffusion and time constant is of the order of 10^8 s. The time constant value increases with time, because the time dependent value of resistance R_2, responsible for the self-discharge of diffuse capacitance increases with time as well.
The voltage on terminals decrease after the short time charging is mainly driven by the charging of the Diffuse capacitance. Time constant of the Diffuse capacitance charging is about 200 s. The Diffuse capacitance is about one half of the Helmholtz one. These results are important from the point of view of supercapacitor equivalent circuit modeling for the estimation of the equivalent circuit parameters values.

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